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DOCUMENT-IDENTIFIER: US 6514394 B1
TITLE: Sensor for application in molten metals

Brief Summary Text (4):
An electrochemical sensor, in particular able to measure the aluminium concentration in a molten metal, is known from patent application EP 0 493 878 A2. The sensor comprises a gas tight holder fabricated of quartz or pyrex with a projection attached to the tip, which is removable by snapping in use to allow the enclosed ion-conducting material or electrolyte to contact the molten metal. NaCl--AlCl.sub.3 electrolyte is used as the ion-conducting material whereby the NaCl acts as saturated solid component. A pure aluminium wire immersed in the ion-conducting material is used as the reference electrode, whereas the molten metal itself serves as the measuring electrode. In a particular embodiment of the invention, a dense .beta.-alumina membrane immersed in the ion-conducting material separates the reference and measuring electrodes. If the composition of the electrolyte remains constant, the aluminium activity at the reference electrode is fixed and known, and if the aluminium activity at the measuring electrode in the molten metal is established, the sodium activity at both sides of the membrane will be known and the value of the aluminium activity at the measuring side can be determined by the following equilibrium: 3 Na+AlCl.sub.3 =3 NaCl+Al. A sodium concentration cell is obtained. By measuring the EMF of this sodium concentration cell, the aluminium activity or concentration in the molten metal can be deduced from Nernst's equation.

Brief Summary Text (6):
Other publications are "Immobilised Molten Salt Membrane based Magnesium Sensor for Aluminium-Magnesium Melts", Vangrunderbeek et al., Ionics 1 (1995) p. 59-62, and "Electrochemical Sensor for Measuring Magnesium Content in Molten Aluminium", Zhang et al., Journal of Applied Electrochemistry, 26 (1996), 269-275. These documents describe sensors for measuring the Mg activity in Al--Mg melts. Disadvantage of said sensors is the insufficient sealing of said sensors with cements for use in an industrial process.

Brief Summary Text (12):
The porous support preferably has porosity between 20 and 50%, most likely between 30 and 40%. As porosity is higher the strength of the porous support will be lower, leading to a limited applicability in an industrial process. When porosity is too low, the conductivity of the impregnated halide will be negatively influenced resulting in an increase of the reaction time of the sensor upon immersion in the molten metal and in a decrease of the obtained accuracy. When the porosity and the pore size are measured by a Coulter Porometer.RTM. and Coulter Porofil.TM. wetting agent, a minimal test gas flow (pressurized air) of 50% should be measured for the pores between 0.5 and 5 .mu.m, most likely between 0.5 and 1.5 .mu.m. The pores are open pores permitting ionic transport. When the average pore size is lower, the ion conductivity of the halide is too low to obtain useful measurements. When the average pore size is higher, the impregnated halide can leave the porous support more easily and the molten metal can penetrated the porous support, making the sensor unclear.

Brief Summary Text (18):

A second main embodiment of this invention is a method to fabricate an electrochemical sensor to measure the activity of a metallic component in a molten metal, comprising the melt as the measuring electrode, a reference electrode, the latter comprising the metallic component to be measured, separated from each other by a liquid ion-conducting halide comprising the metallic component to be measured and immobilized in a non-conducting porous support fabricated from a material substantially inert to the molten metal, the halide and the reference electrode material and wherein the reference electrode contains an external connection consisting of an electrically conducting wire in an electric isolating protection material, chemically substantially inert, characterised in that the method is built up according to the following sequential steps: sealing of the porous support containing the reference electrode material and the external connection, using a high temperature cement, immobilizing the halide into the porous support at a temperature above the melting temperature of the reference electrode material or melting of the electrode material followed by immobilizing the halide into the porous support at a temperature lower than the melting temperature of the reference electrode material so that in both cases the reference electrode material is introduced by melting the reference material inside the electrochemical sensor, sealing of the external connection of the reference electrode above the melt using a gas tight paste, and in-situ completion of the sealing of the sensor by totally immersing the porous support of the sensor under the melt surface.

Detailed Description Text (2):
FIG. 1 schematically describes the sensor according to the invention being completely immersed in the molten metal. In FIG. 1, (1) is the porous support impregnated with a halide, (2) the reference electrode, (3) a high temperature cement, preferably zirconia based, to seal the porous support, (4) an electric wire for the reference electrode, (5) a ceramic tube to protect the electric wire of the reference electrode, (6) vacuum paste for the ceramic tube preferably with a leak rate better than 10.sup.-6 mbar liter sec.sup.-1, (7) an electric wire for the measuring electrode, (8) a tube made of a ceramic or refractory material, and (9) the surface of the molten metal.

Detailed Description Text (14):
permeates the support. The grain size distribution of the MgO powders was 325 mesh. The halide that was impregnated consisted of MgCl.sub.2 --KCl with a molar ratio of 4:1.

Other Reference Publication (1):
Vangrunderbeek et al., "Immobilised Molten Salt Membrane based Magnesium Sensor for Aluminum-Magnesium Melts," Ionics, 1 (1995), month unavailable, pp. 59-62.

CLAIMS:

23. A method of producing an electrochemical sensor to measure the activity of a metallic component in a melt comprising: a measuring electrode comprising tie melt; a reference electrode comprising i) the metallic component whose activity is to be measured, ii) an external connection comprising an electrically conducting wire held in an electrically isolating material which is substantially chemically inert to the melt and the reference electrode, and has a gas tight seal above the surface of the melt, and iii) a high-temperature-cement, wherein the reference electrode is sealed from the air by the melt, the high temperature-cement, the gas tight sealing of the external connection above the melt, and by melting the reference electrode inside the porous support; and a liquid ion-conducting halide that separates the measuring electrode and the reference electrode, wherein the liquid ion-conducting halide comprises the metallic component to be measured; and a non-conducting porous support that immobilizes the liquid ion-conducting halide, wherein said porous support is fabricated from a material that is substantially chemically inert to the melt, the halide, and the reference electrode, wherein the method comprises the steps of: a) sealing the porous support containing the reference electrode material

and the external connection, by means of a high temperature cement; b) immobilizing the halide into the porous support at a temperature higher than the melting temperature of the reference material, or melting the reference electrode material inside the electrochemical sensor followed by immobilizing the halide into the porous support at a temperature lower than the melting temperature of the reference electrode material by which in both cases the reference electrode material is introduced by melting the reference electrode material inside the electrochemical sensor; c) sealing the external connection of the reference electrode by a gas tight paste above the melt; and d) totally immersing in the melt that part of the sensor containing the porous support, thereby completing, in-situ the sealing of the sensor.